

Hole sp^3 -character and delocalization in (Ga,Mn)As

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The most investigated dilute magnetic semiconductor (Ga,Mn)As is believed to be ferromagnetic due to the p-d Zener model, with the interactions mediated by extended holes in the valence bands, since the work by T. Dietl et al. [Science **287**, 1019 (2000)]. Recent experimental work by M. Dobrowolska et al. [Nature Mater. **11**, 444 (2012)] presents a diverse view with the holes localized within the Mn-3d derived impurity states. In this work, we investigate this system applying the density functional theory (DFT) with the pseudopotential self-interaction correction (pSIC) and maximally localized Wannier functions (MLWFs). Our results clearly show the sp^3 character of a hole introduced by the substitution of Ga with Mn. Contribution of the Mn-3d states to that hole amounts to 3-12% depending on the method and doping level between 1% and 3%. Very extended nature of this hole, ranging beyond the second shell of the As-neighbors along the 110-axis, confirms by means of the ab-initio methods well established mechanism of the ferromagnetic order in this system. Under low doping of 1%, the Fermi level is still pinned to the valence band, and the impurity states within the gap are spin unpolarized and of the s-type.

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Dilute magnetic semiconductors (DMS) possess combined semiconducting and magnetic properties, hence their potential application in spintronics have been extensively investigated over past 30-years.¹⁻⁵ A prototype DMS used to explain a mechanism of the ferromagnetic order in these class of materials is (Ga,Mn)As. It is a half-metal in majority-spin band with a spin-polarized hole introduced to the host GaAs by a substitution of Ga with Mn. The nature of this hole rules magnetic and transport properties. Therefore, deep understanding of a type and localization of empty states near the Fermi level and within the energy gap is a subject of hot debate.

In the pioneering work, Dietl et al.^{6,7} assumed the extended-hole scenario, with a hole delocalized within the valence band, and applied p-d Zener model to successfully explain high Curie temperature, reaching 110 K, in GaAs with 5% of Mn. Since then, many papers based on this model have been written and very intensive ab-initio studies on the (Ga,Mn)As system have been performed.

Recently, a contradicting hypothesis, with a hole captured within the localized Mn-3d impurity states, is pursued in the experimental group and published in the work by Dobrowolska et al.⁸ These beliefs are mainly based on transport, magnetization and magnetic circular dichroism measurements for very weakly doped samples in the insulating state, where holes appear to be trapped in very localized states within the energy gap. Following the above experimental suggestions, a theoretical model based on the first-principles calculations have been proposed for the ferromagnetism determined by the impurity band, on both the metallic and dielectric sides of the metal-insulator transition.⁹ Previous work by these authors sounds differently.¹⁰

Our results, presented in this work, clearly demonstrate that the above suggestions about the hole being localized within the impurity band are wrong. The hole

is very extended over both the 3d- and 4p-states of Mn and over the As atoms, even far away from the impurity. Its character is mainly dominated by the sp^3 hybridizations centered on four As atoms neighboring to the Mn impurity, and this holds for both the metallic and the quasi-insulating cases.

We performed the calculations within the density functional theory¹¹ (DFT) framework, employing the QUANTUM ESPRESSO code,¹² with the pseudopotentials (PPs) and the plane-wave basis. For the exchange - correlation functional, we chose the generalized gradient approximation (GGA) by means of the Perdew-Burk-Erzenhof parametrization.¹³ We used the ultrasoft pseudopotentials¹⁴ with the semicore 3s- and 3p-shell of Mn and the 3d-shell of Ga included in the valence bands, and with nonlinear core correction for the Ga and the As PPs. The energy cutoffs of 35 Ry and 350 Ry were set for the plane-waves and the density, respectively. The calculations were done for two Mn concentrations: 1% with one Mn atom in the 216-atoms cell and 3% with a single impurity in the 64-atoms cell. Dense k-point grids of (6,6,6) and (12,12,12) points generated according to the Monkhorst and Pack scheme¹⁵ were used, for these dopings respectively. For a quadrature over the Brillouin zone, the metallic-smearing technique¹⁶ close to the Fermi surface was used with the gaussian broadening of 0.01 Ry. The experimental lattice constant of 5.65 Å was fixed for all calculations, and the atomic positions in the cells were optimized. The largest relaxation, found close to the Mn impurity, was smaller than 0.6% of the Ga-As bondlength.

For a better treatment of the exchange-correlation interactions, the pseudopotential self-interaction corrected (pSIC) scheme^{17,18} was also applied and compared to the GGA results. To imagine a character of the hole and its shape in the real space, we calculated the maximally lo-

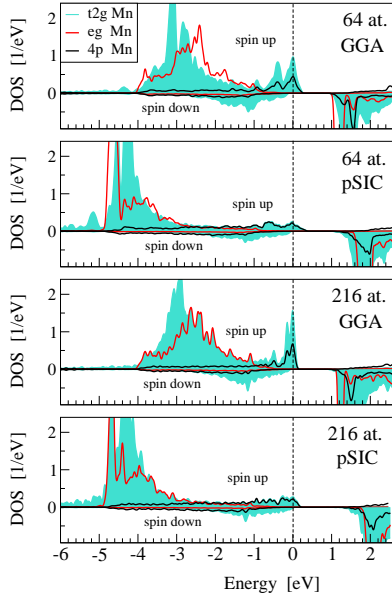


FIG. 1. (Color online) Projected density of states (DOS) for t_{2g} , e_g and $4p$ states of Mn in (Ga,Mn)As at doping levels of 3% (64-at. cell) and 1% (216-at. cell). The Fermi level is marked by the vertical dotted-line.

calized Wannier functions (MLWFs)¹⁹ using the wannier code.²⁰ Hole localization degree can be estimated from the MLWFs spreads, Ω_n , defined as:¹⁹

$$\Omega_n = [\langle r^2 \rangle_n - \bar{\mathbf{r}}_n^2], \quad (1)$$

where $\bar{\mathbf{r}}_n^2 = \langle 0n | \mathbf{r} | 0n \rangle^2 = \langle \mathbf{r}_n \rangle^2$ and $\langle r^2 \rangle_n = \langle 0n | r^2 | 0n \rangle$, with $|0n\rangle$ being the Wannier function with number n and centered in the original cell with the direct-lattice vector $\mathbf{R} = 0$, and \mathbf{r} is the real-space position operator. The sum of above defined quantities $\Omega = \sum_n \Omega_n$ is minimized in the MLWFs-finding procedure.¹⁹

The Mn impurity, replacing Ga in the GaAs host, offers two electrons from the $4s$ -shell and five electrons from the $3d$ -shell instead of the Ga configuration $4s^2 3d^{10} 4p^1$. Since the valency of As is 5 and that of Ga is 3, the substitution of Ga with Mn creates a hole in the valence band, because five $3d$ electrons of Mn almost do not take a part in binding with the As neighbors. We will prove this statement here.

In Figure 1, the density of states (DOS) projected on the t_{2g} , e_g and $4p$ Mn-orbitals is presented. The Fermi level cuts through the valence band top, for two concentrations and both theoretical methods applied. The DOS center of mass, for the t_{2g} and e_g states, moves in the pSIC scheme energetically downwards in comparison to the GGA. Also, the number of states at the Fermi level decreases in the pSIC. These results are consistent with the previous pSIC calculations²¹ and the LDA+U results.^{22,23} The e_g -shell in spin up (\uparrow) is fully occupied, and the t_{2g} (\uparrow) states are almost completely filled, with Löwdin's occupation analysis²⁴ giving 2.74-2.85. The spin-down (\downarrow) states are quite empty for the

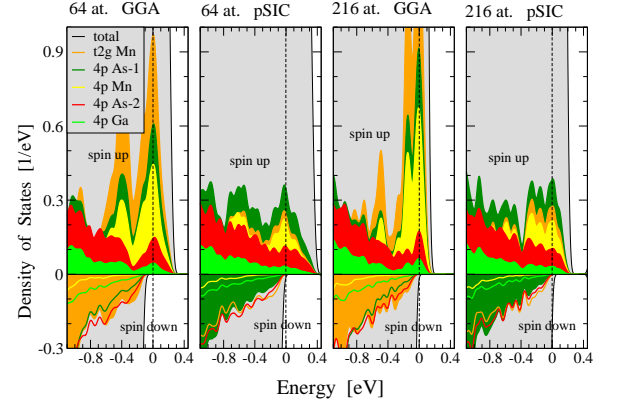


FIG. 2. (Color online) Projected density of states (DOS) close to the Fermi level at dopings of 3% and 1%, obtained within the GGA and the pSIC. The total DOS is marked by the grey color and ranges beyond the scale. As-1 and As-2 denote the first- and second-neighbor As-atoms along the Mn-As-Ga-As chain in 110-direction, the Ga-atomic site is $(1/2,1/2,0)$ in units of the lattice constant and Mn is at the origin.

TABLE I. Contribution to the hole occupations, n_h , from the projected DOS [in %], for two doping levels: 3% and 1%, obtained within the GGA and the pSIC. Wyckoff positions in the cells in units of the lattice constant are given in parenthesis. The sum of contributions from Mn and its neighbors along four tetragonal easy-axes are given in the last row.

states (atomic position)	64 at.		216 at.	
	GGA	pSIC	GGA	pSIC
t_{2g} -Mn (0,0,0)	10.75	4.65	11.10	3.03
$4p$ -Mn (0,0,0)	4.97	4.05	4.78	2.34
$4p$ -As (1/4,1/4,1/4)	7.17	7.18	6.67	4.41
$4p$ -Ga (1/2,1/2,0)	0.52	0.65	0.47	0.36
$4p$ -As (3/4,3/4,1/4)	2.05	2.89	1.34	1.32
total from 4 easy axes	54.68	51.58	49.80	29.73

Mn- $3d$ states, with Löwdin's occupations of 0.52-0.72 for the t_{2g} . Total magnetization in the cell is about 4.0-4.2 μ_B for all methods and Mn concentrations. Absolute magnetization is much higher, 4.86-5.36 μ_B , also due to substantial polarization of neighboring As atoms, 0.07 μ_B , coupled antiferromagnetically to the impurity moment.

Closer perspective at the Fermi-level region of the DOS projected onto $3d$ - and $4p$ -Mn states, and onto $4p$ -states of neighboring atoms from the Mn-As-Ga-As chain along the 110 axis, is presented in Figure 2. For accuracy, Table I collects the hole occupation numbers, n_h , obtained from a quadrature of the projected DOS, $N(\varepsilon)$, in a range from the Fermi level, ε_F , to the energy at which the DOS vanish first time for the unoccupied states,

$$n_h = \int_{\varepsilon_F}^{\varepsilon_{N(\varepsilon)=0}} N(\varepsilon) d\varepsilon. \quad (2)$$

We conclude, that the hole is composed of many states:

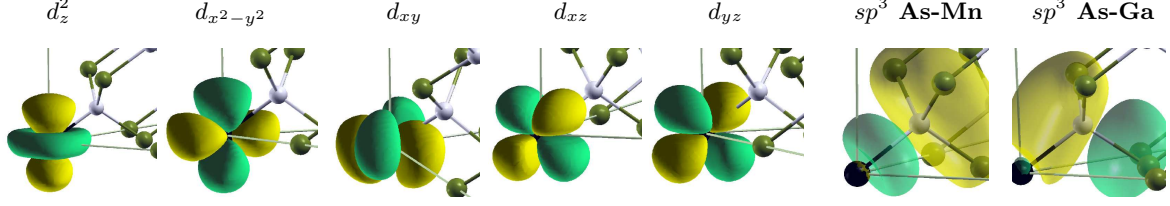


FIG. 3. (Color online) Maximally localized Wannier functions, for the spin up, centered at Mn and the neighboring As atom, obtained for the 64-atoms cell with the GGA. The sp -lobes along the As-Mn and As-Ga bonds were chosen from a manifold of sp^3 hybridization. All functions were plotted with the same isovalues. The Mn atoms are depicted in back color, As in white and Ga in olive color.

TABLE II. Spreads of the MLWFs, Ω_n [in \AA^2], obtained for the occupied states, by means of the GGA and the pSIC, for (Ga,Mn)As in the 64-atoms cell (doping 3%) and for the atomic Mn and pure GaAs. Numbers of symmetry-equivalent sp -lobes are in parenthesis. Spin channels are denoted by up- and down-arrows.

functions	GGA	pSIC
Mn: d_{z^2} , $d_{x^2-y^2}$ (\uparrow)	0.77	0.69
Mn: d_{xy} , d_{xz} , d_{yz} (\uparrow)	1.20	1.01
Mn atom: d^5 (\uparrow)	0.46	0.46
Mn-As: sp^3 (\uparrow)	2.82 ⁽¹⁾ 3.54 ⁽³⁾	2.95 ⁽¹⁾ 3.75 ⁽³⁾
Mn-As: sp^3 (\downarrow)	2.48 ⁽¹⁾ 3.30 ⁽³⁾	2.74 ⁽¹⁾ 3.42 ⁽³⁾
Ga-As (central): sp^3 (\uparrow)	3.35 ⁽¹⁾ 3.29 ⁽³⁾	3.64 ⁽¹⁾ 3.58 ⁽³⁾
Ga-As (central): sp^3 (\downarrow)	3.36 ⁽¹⁾ 3.30 ⁽³⁾	3.64 ⁽¹⁾ 3.58 ⁽³⁾
pure GaAs: sp^3	3.15 ⁽⁴⁾	3.59 ⁽⁴⁾

a contribution of the Mn-3d states is the highest by means of the GGA, and the maximal weight from the As-4p states of the first impurity neighbors results from the pSIC. If we take into account the fact that there are four nearest neighbors of Mn, then it is obvious that the hole is mainly located around the impurity neighbors and not at the impurity. The Mn-4p donation to the hole is almost as high as from the Mn-3d states (pSIC) or about half of the Mn-3d input (GGA). Interestingly, the hole extends beyond the second As-neighbors of Mn, and only half, or less, of the hole occupation is summed over the Mn atom and its twelve neighbors from the Mn-As-Ga-As chains along four easy axes.

Chemical bond of Ga with As-neighbors is built by 4s and 4p electrons. For the Mn impurity, occupations of the 4s-states are about 0.34 (\uparrow) and 0.27 (\downarrow) for both the GGA and the pSIC, and for the 4p-states the corresponding numbers are 0.70 (\uparrow) and 0.50 (\downarrow) (GGA) 0.89 (\uparrow) and 0.60 (\downarrow) (pSIC), independently of impurity concentrations. To get a closer insight into the Mn-As bonds, we calculated the MLWFs on the GGA and the pSIC Bloch-functions obtained for the 64-atoms cell. For minimization of the total spread, we chose the 133- and 128-band

space in the spin up and down, respectively. Bottom of the energy window was set within the gap between the localized 3d-Ga derived bands and the delocalized sp -bands of (Ga,Mn)As. Top of the energy window was fixed just above the 133-rd band counted for the spin up from the bottom of the energy window. From this band-manifold, we obtained 133 and 128 MLWFs in the spin up and down, respectively. They are of the sp^3 -character centered closely to each of 32 As atoms in the cell (exactly slightly on the backbonds As-Ga and As-Mn) and the d^5 -type centered at Mn. Because of the chosen energy window, the obtained Wanniers contain the hole. Plots for some MLWFs for the spin-up channel, obtained with the GGA, are drawn in Figure 3. Spreads, Ω_n , of some representative MLWFs for (Ga,Mn)As, obtained from the GGA- and the pSIC Blochs, are collected in Table II and compared to the MLWFs obtained for isolated Mn and pure GaAs.

It is clear, that characters of the sp -lobes on the Mn-As bonds are very similar to those on the As-Ga bonds, except slightly smaller spreads of the As-Mn MLWFs caused by a little shift away from Mn. The Mn-3d MLWFs are much more localized than the sp^3 -functions. Although, spreads of the d -type functions are twice, for e_g , and three times, for t_{2g} , larger than for the corresponding functions of the isolated atom. Plots also show that a contribution of the t_{2g} -symmetry functions to the As-Mn bond is small, and even with a tendency to escape from the bondline, as one can see from an asymmetry of plus- and minus-sign lobes of the d_{xy} MLWF (d_{xz} and d_{yz} have the same property). Spreads of the sp^3 MLWFs on the As-Ga bonds in (Ga,Mn)As are larger than these in pure GaAs, like Mn-substitution effect was blowing them. It might be a signature of the hole being localized close to the As atoms. Finally, an effect of the pSIC shows better localization around atoms. This causes decrease of atomic spreads, and increase of the distance between lobes of the interatomic MLWFs, and decrease of covalency. When bands are infinitely thin, and there is no k-points dispersion, then an effect of the pSIC on the MLWF-spreads is vanishing.

Importantly, taking a closer look at the hole bandwidth, i.e. $[\varepsilon_F, \varepsilon_{N(\varepsilon)=0}]$, for different dopings, we find

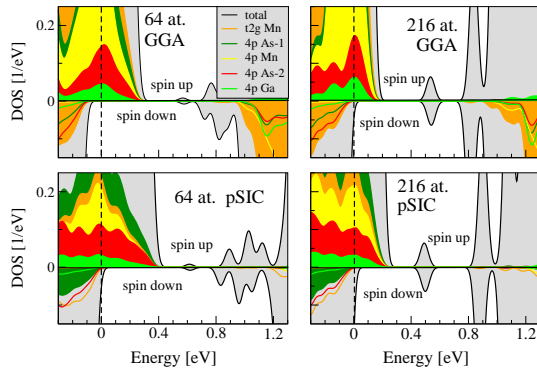


FIG. 4. (Color online) Total density of states (DOS) close to the Fermi level (marked by the vertical dotted-line) and within the energy gap of (Ga,Mn)As, obtained with the GGA and the pSIC, at 3% and 1% dopings.

that none case seems strictly insulating. For 3% of Mn, the hole bandwidth is 0.3 eV (GGA) or 0.4 eV (pSIC), and for 1% of Mn, it amounts to 0.18 eV (GGA) or 0.28 eV (pSIC). Experimentally, the samples below 1% of Mn appear insulating, due to very thin bandwidths above the Fermi level. Theoretically, there is no segregation of the DOS from the top of the valence bands, as some authors suggest.^{8,9} For very low doping, the impurity band within the gap originates from the conduction states. It is not obvious just from the DOS, but counting electrons and bands in the system, we are sure about

this. Detailed picture of the gap region is included in Figure 4. Composition of the impurity band within the gap, for the 216-atoms cell and for both the GGA and the pSIC, consists of the 4s-functions of Mn, As and Ga atoms, and there is no *d*- or *p*-type add. Anyway, due to their small bandwidths, the impurity states can act as a trap for electrons from the Mn interstitials, which are known to be donors,²⁵ or these bands can be populated via absorption of photons.

Concluding, we have demonstrated that the hole in (Ga,Mn)As is very delocalized, and it has mainly *sp*³-character centered on the As-neighbors of Mn. For very low dopings, the impurity band within the gap forms via a segregation from the conduction states, and it is purely of the *s*-type. Fermi level is pinned within the valence band for both the metallic and the quasi-insulating cases. Models for Curie temperature in (Ga,Mn)As, whose assume an extended hole over the valence band,^{7,26,27} are clearly justified.

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